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(21) International Application Number: PCT/EP92/00245 (22) International Filing Date: 4 February 1992 (04.02.92) (30) Priority data: 9102513.0 6 February 1991 (06.02.91) GB (71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS INC. [US/US]; 200 Park Avenue, Florham Park, NJ 07932 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): HAMARD, Jacques, Marie, Michel [FR/BE]; Avenue Fond-de-la-Vigne 23, B-1330 Rixensart (BE). (74) Agents: BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P. O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), CS, DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), PL, RU, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: ALCOHOL PRODUCTION (57) Abstract Nonyl alcohol is obtained by oxonation of an octene with a low content of triple branched isomers produced by catalytic dimerization of butene under conditions of high temperature and high conversion rates.		

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ALCOHOL PRODUCTION

This invention relates to the manufacture of alcohols from particular higher molecular weight olefins obtained from lower molecular weight olefins by catalytic polymerization using a solid phosphoric acid catalyst and is concerned more—especially with the manufacture of nonyl alcohols from octenes obtained by dimerization of butenes. The invention also relates to esters of the alcohols and the use of the esters as plasticizers.

It has long been known - see for example "Advances in Catalysis and Related Subjects", Volume 8, pp 219 to 238 (Edwin K. Jones), Academic Press Inc., 1956 - to convert butenes optionally mixed with propene, using a phosphoric acid catalyst, to octenes and heptenes for use, usually after hydrogenation and addition of tetraethyl lead, in gasoline. Although other materials have been used for catalysing polymerization, or oligomerization, reactions of this type, solid phosphoric acid catalysts are predominantly employed use of their tolerance to impurities that poison other catalysts, for example sulphur, acetylenic hydrocarbons, oxygen-containing compounds, and water, the necessity for the removal of which makes the use of other catalysts economically unattractive. Solid phosphoric acid catalysts are accordingly used in the present invention.

Although much of the published prior art describes gasoline, alkylarylsulphonate detergents, and alkylbenzens as end uses of the polymerization products, they may also be used as feedstock to the oxo process, the resulting aldehydes being oxidized to acids or hydrogenated to form alcohols, which latter are in turn esterified to form plasticizers, for example dioctyl and dinonyl phthalates.

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In British Specification No. 477128 it is pointed out that the severity of polymerization conditions, as measured by reaction time and temperature, required for reaction increases progressively through the series isobutene, n-butenes and propene (although the Jones article cited above mentions that in the presence of butenes, propene is more reactive than the butenes), and that in the case of isobutene the principal product is a compound that on hydrogenation yields 2,2,4-trimethylpentane, the standard by which octane numbers of gasolines are measured. The octane numbers of the polymerization products of n-butenes are lower.

In U.S. Patent No. 3309421, similar observations are made and a distinction is made between 1- and 2-butenes, 2-butene requiring higher temperatures and pressures and lower space rates than 1-butene to effect a given conversion. In order to provide gasoline of maximum octane number from a given feedstock, polymerization is effected under conditions that so far as possible minimize reaction of 2-butene relative to 1-butene, unreacted 2-butene being distilled from the reaction product stream and used as feedstock for alkylation, while the polymerizate is hydrogenated to form a gasoline component with the maximum proportion of triply branched material available from the starting material under consideration.

Among other references describing similar reaction conditions and the controls necessary to obtain a desired reaction product for use in the alkylation of benzene may be mentioned U.S. Patent No. 2695326, which describes, in Column 3, Table II, that at a pressure of 1000 psig (70 bar), a feed rate of 0.32 U.S. gal/hr/lb of catalyst ($2.67 \text{ dm}^3/\text{hr}/\text{kg}$) and reaction temperature of 450°F (about 232°C), a feed comprising in mole per cent 21.3% propene, 17.3% n-butenes, 8.9% isobutene, diluted with 5.7% propane and 46.2% butane, yielded a product comprising 28.7% C_7 olefins and 55.4% C_8 to C_{11} olefins.

These references are not concerned with using the olefin for alcohol manufacture or the use of the alcohols in plasticizer production. There is a close, inverse, correlation between plasticizer qualities, especially in relation to the low temperature properties of plasticized poly(vinyl chloride) and the proportion of tribranched molecules in the octene produced by the dimerization process.

It has now been found that alcohols particularly nonyl alcohols for the production of dinonyl plasticizers imparting improved low temperature properties to polymers may be produced by the oxo process of the type described above if the nonyl radical is derived from an octene produced from a chosen butene feedstock under chosen reaction conditions.

The present invention accordingly provides a process for the production of alcohols comprising oxonating an olefin obtained by catalytically dimerizing an olefinic feedstock, comprising butene and optionally propene and containing a molar proportion of butene, based on the total weight of olefins, of at least 50%, and the butene containing at most 55%, advantageously at most 25%, and preferably at most 5% of isobutene, wherein the reaction is maintained at at least 200°C, and advantageously at least 210°C, preferably at least 220°C, but at most at 235°C, measured at the reactor outlet, and the space velocity is at most 0.5 USG/h/lb of catalyst (at most about 4.1 dm³/h/kg of catalyst), the product of the temperature and the proportion by weight of total olefins converted advantageously being at least 200, and preferably at least 210 and hydrogenating the product of oxonation.

This product is referred to subsequently herein as "severity". It is preferred that the proportion by weight of total olefins converted is at least 0.90, advantageously 0.95, and preferably at least 0.97.

Advantageously, the pressure within the reactor is within the range of 500 to 1200 P.S.I. (about 3.45 to 8.27 mPa) and space velocity is preferably in the range of 0.1 to 0.4 USG/h/lb (about 0.8 to 3.3 dm³/h/kg).

We have found that using such a dimerization process minimises the proportion of tribranched octenes in the product and can maintain the tribranched octenes at a level of at most 20%, advantageously 15%, more advantageously 12%, and preferably 10%, of the total octene in the product.

The reaction conditions to obtain octenes with the desired tribranched component will depend primarily on the proportion of butene in the olefin component of the feed, and the proportion of iso-butene in the butene component. It may, however, be generally stated that

- (a) the higher the proportion of butenes in the olefin the higher the required severity
- (b) the higher the proportion of iso-butene in the total butene, the higher the required severity
- (c) as the catalyst loses activity as the reaction proceeds, to maintain the required severity it is necessary to reduce space velocity and/or increase temperature, up to the maximum temperature (235°C) specified above.

The proportion of total olefins produced represented by all isomers of octene (selectivity to octene) is reduced with an increase in severity.

The octene quality is improved both with higher olefin conversion and with temperature and these effects become more marked as the proportion of butene in the feed is increased.

As catalyst there is used a solid phosphoric acid catalyst, comprising a phosphoric acid, e.g., ortho-, pyro-, meta- or poly-phosphoric acid, on a solid carrier. The carrier may, for example, be a synthetic or natural porous silica or other oxide-containing material, e.g., keiselguhr, kaolin, infusorial earth, diatomaceous earth, activated clay, a zeolite, or an oxide of aluminium, zirconium, titanium or thorium. The acid is blended with the carrier to form a paste, and the paste may then be calcined and the resulting mass crushed or the paste may be extruded and pelletized and then calcined to yield uniform catalyst particles.

The catalyst may contain other components, for example, mineral talc, fullers earth, and various metals or their oxides or phosphates or pyrophosphates, e.g., nickel, copper, cobalt, zinc, manganese and, especially, iron, to modify its activity or physical properties, e.g., thermal conductivity, strength and attrition resistance.

The solid phosphoric acid catalyst advantageously contains 50 to 90% by weight of phosphoric acid.

As indicated above, the activity of the catalyst gradually falls as the reaction proceeds, and under given conditions the proportion of olefins converted accordingly falls. The feedstock may be contacted with catalyst of different activities, either successively, in different reactors, in which case the reaction conditions in different reactors may differ, or a blend of different catalyst may be employed. Catalysts at three different levels of activity may conveniently be employed.

During operation, the catalyst is advantageously kept hydrated, which reduces the rate of loss of activity. This may be conveniently accomplished by incorporating small quantities of water in the olefin feedstock, e.g., from 500 to

3000 parts per million.

Advantageously, the olefin feedstock to the dimerization reaction also contains paraffins, preferably butanes, which being unreactive act as diluents and reaction solvents, and hence temperature, control agents, the oligomerization reaction being exothermic.

The method of the invention is applicable to diene-containing feedstocks, especially those containing up to 5000 ppm diene.

In a further embodiment of the oligomerization method, an olefin feedstock containing propene and butene is divided, as by distillation, into a relatively propene-rich stream and a relatively butene-rich stream, the butene-rich stream is divided into a relatively isobutene-rich stream and a relatively n-butene rich stream, and the last-mentioned stream subjected to oligomerization as defined above. By this procedure, in which propene and butenes are separated, it is possible to maximize production of desired nonenes and octenes from a mixed C_3/C_4 feedstock.

Further, by maintaining a reduced level of isobutene in the feed, the catalyst life may be prolonged.

It will be understood that the octene of the invention is a mixture of isomers, as will be the downstream products of the invention.

The product resulting from oligomerization is fractionated, if required, and the fraction containing the octene subsequently be subjected to the oxo process, hydrogenation and esterification to yield a plasticizer, e.g., dinonyl phthalate. These are carried out by methods known per se and will not be described in detail here.

Conventional oxonation conditions may be used in the process of this invention and the operating temperatures, pressures and other conditions, such as synthesis gas composition, may be controlled in accordance with the usual expertise of the person skilled in the art to maximise yield of the desired alcohol. For example, the hydroformylation reaction may be carried out at a pressure of 150-300 atm, and a temperature of from 120°C to 190°C.

The catalyst may be used in desired active form for example in a concentration of from 0.05-3 wt% preferably 0.05 and 1 wt% as metal, preferably cobalt, based on the olefinic feed. Typically the synthesis gas used might have a H₂:CO volume ratio in the range 0.9:1-1.5:1.

The oxonation reaction typically produces mixtures of alcohols and aldehydes. In order to increase the alcohol yield the product of oxonation is hydrogenated where higher alcohol passes through unconverted, the higher aldehyde is converted to higher alcohol, and the olefinic hydrocarbon is either reduced or, as with saturated hydrocarbons, passes through unchanged: at the subsequent distillation stage the higher alcohol is removed as the desired product of the overall process.

Any conventional hydrogenation techniques may be used. In a preferred process the oxonation product is fed to a conventional hydrogenation train where, using Cu/Cr and Ni catalysts, a hydrogen pressure of 50 bars and a temperature of 120-170°C the product containing higher aldehydes, formates and acetals was converted to a hydrogenation product mixture containing the desired higher alcohol.

The invention accordingly also provides an ester of the resulting alcohol, more especially a phthalate ester of nonyl alcohol.

The invention further provides a polymer composition, comprising a polymer, more especially a vinyl chloride homo or copolymer, and an ester according to the invention, more especially a phthalate ester.

The following Examples illustrate the invention:

Example 1

Using a solid phosphoric acid catalyst from U.O.P. Inc., a feedstock having the following composition was polymerized under the conditions given.

Feedstock Composition

<u>Component</u>	<u>%, by volume</u>
propylene	0.2
1-butene	22.8
isobutene	1.6
2-butene	25.4
saturates	50.0

Reaction Conditions

Reactor Temperature, Inlet, °C	207
Outlet, °C	232
Pressure, MPa	6.9
Space Velocity, dm ³ /h/kg	2.17
Butene Conversion, %	99.9

The olefin product was as follows:

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Carbons	5-6	7	8	9	10	11	12	13+
wt%	2.8	4.7	40.2	12.4	6.2	6.8	20.1	6.8

The percentage composition of the octene was as follows:

Linear	1.7
One branch	24.4
Two branches	63.4
Three branches	10.5

The product was distilled, and a fraction boiling in the range 104° to 135°C was obtained, representing a 43% weight yield on butene, of the following composition:

Carbon Number	7	8	9
wt%	2.9	86.4	10.7

The fraction was oxonated and reduced, and the resulting alcohol esterified with phthalic anhydride to produce diisononyl phthalate.

The diisononyl phthalate was used at a level of 50 parts per hundred parts of resin to produce a plasticized poly(vinyl chloride), the properties of the formulation being compared with polymer plasticized with (A) di-2-ethylhexyl phthalate and (B) a diisononyl phthalate produced from a triply branched octene.

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<u>Plasticizer</u>	<u>Example 1</u>	<u>Comparison</u>	
		A	B
100% modulus, MPa	11.4	10.3	12.8
Low Temperature Flexibility, Clash Berg, °C	-27	-29	-17
Soap Solution, % Loss	1.1	5.0	2.0

Examples 2 to 9 are other illustrations of the production of low triple branched octenes suitable for conversion into nonyl alcohol useful for the production of improved dinonyl phthalate plasticizers.

Example 2

The procedure of Example 1 was repeated, using the same feedstock and the same butene conversion rate, the reaction conditions being varied as follows:

Reactor Temperature, Inlet, °C	204
Outlet, °C	216
Pressure, MPa	4.1
Space Velocity, dm ³ /h/kg	1.25

The percentage composition of the resulting octene was:

Linear	2.6
One branch	27.5
Two branches	63.7
Three branches	6.1

Example 3

The procedure of Example 2 was repeated, with the reactor temperature varied as follows:

Inlet, 192°C; Outlet, 204°C

The percentage composition of the resulting octene was:

Linear	1.1
One branch	20.9
Two branches	68.4
Three branches	9.6

Example 4

This example illustrates the effect of varying the olefin conversion rate on the proportion of triply branched octenes in the product. An olefinic feedstock containing propene and butene (48 mole% butene; isobutene 51.78% of total butene content) was passed over a solid phosphoric acid catalyst at a pressure of 1000 psi (6.89 MPa) with a reactor outlet temperature of 420°F (216°C) at varying space velocities and olefin conversion rates. The results are shown below:

Space Velocity	Conversion Rate	C ₈ Triple Branched
dm ³ /h/kg	%	%
2.5	93.6	7.6
2.5	97.9	4.37
2.5	98.2	3.72
4.17	96.9	7.18
4.17	97.3	7.02

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Example 5

This example illustrates the effect of varying the reactor outlet temperature on the triply branched octene proportion. The feedstock contained propene and butene (46.7 mole% butene; isobutene 50.91% of total butene); pressure as in Example 4, space velocity 2.5 dm³/h/kg.

<u>Outlet</u> <u>Temperature, °C</u>	<u>Olefin</u> <u>Conversion, %</u>	<u>Triply</u> <u>Branched, %</u>
204	98.5	10.64
215	98.4	5.32

Example 6

The procedure of Example 5 was repeated on a feedstock containing propene and butene (79.3 mole% butene; isobutene 51.16% of total butene), pressure as in Example 4, space velocity 2.5 dm³/h/kg.

<u>Outlet</u> <u>Temperature, °C</u>	<u>Olefin</u> <u>Conversion, %</u>	<u>Triply</u> <u>Branched, %</u>
215	97.3	20.33
232	97.5	9.15
232	97.7	8.58

The results show that increasing reactor temperature significantly reduces triple branching, while an increase in olefin conversion rate also improves the product.

Example 7

This example shows the effect of changing the propene:butene ratio in the feedstock. Reaction conditions as in Example 4, space velocity 2.5 dm³/h/kg.

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<u>C4, %</u>	<u>iso-C4 on C4, %</u>	<u>Conversion %</u>	<u>Triple Branched %</u>
49.5	52.55	97.5	4.92
78.7	51.02	97.7	28.56

Example 8

This example shows the effect of pressure on triple branching. The feedstock was propene and butene; butene 78.7%, isobutene on total butene 51%, reactor outlet temperature 215°C, space velocity 2.5 dm³/h/kg.

<u>Pressure MPa</u>	<u>Conversion, %</u>	<u>Triple Branching, %</u>
4.83	97.1	26.81
6.89	97.13	12.73

Example 9

This example demonstrates the concept of severity, the product of reactor outlet temperature and olefin conversion proportion (fraction). An olefinic feedstock containing equimolar proportions of propene and butene, with an isobutene content 21% of total butene, was oligomerized over a solid phosphoric acid catalyst at various reactor outlet temperature and olefin conversion rates.

<u>Reactor Outlet, °C</u>	<u>Olefin Conversion</u>	<u>Triple Branching, %</u>	<u>Severity</u>
204	0.839	23.1	171
204	0.937	17.3	191
218	0.865	15.8	189
218	0.958	10.8	209
232	0.908	11.2	211
232	0.972	5.6	226

The practically linear inverse relationship between severity and triple branching, clear from the table, enables reactor

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temperature or olefin conversion rate to be adjusted to yield an octene product having a sufficiently low proportion of triply branched isomers.

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CLAIMS:

1. A method for the production of alcohols comprising oxonating an olefin obtained by oligomerizing in the presence of a solid phosphoric acid catalyst an olefinic feedstock comprising butene and optionally propene, and containing a molar proportion of butene, based on the total olefin content, of at least 50%, and the isobutene content of the butene being at most 55%, wherein the reactor outlet temperature is maintained within the range of from 200°C to 235°C, the space velocity is at most 4.1 dm³/h/kg of catalyst and hydrogenating the product of oxonation.
2. A method according to claim 1 in which the proportion by weight of olefin oligomerized is at least 0.90.
3. A method as claimed in claim 1 or claim 2, wherein the isobutene content of the butene is at most 25%.
4. A method as claimed in any one of claims 1 to 3, wherein the reactor outlet temperature is at least 210°C.
5. A method as claimed in any one of claims 1 to 4, wherein the proportion of olefin oligomerized is at least 0.95.
6. A method as claimed in claim 5, wherein the said proportion is at least 0.97.
7. A method as claimed in any one of claims 1 to 6, wherein the product of the reactor outlet temperature and the proportion of olefin oligomerized, i.e., the severity, is at least 200.

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8. A method as claimed in claim 7, wherein the severity is at least 210.

9. A method as claimed in any one of claims 1 to 8, wherein the olefinic feedstock contains a saturated hydrocarbon diluent.

10. A method as claimed in claim 9, wherein the diluent is propane, butane, or a mixture thereof.

11. A method as claimed in any one of claims 1 to 10, wherein the catalyst is a blend of solid phosphoric acid catalysts of differing activity.

12. A method as claimed in any one of claims 1 to 11, wherein catalyst activity is maintained by an effective proportion of water in the feedstock.

13. A method as claimed in any one of claims 1 to 12, wherein the feedstock is obtained from a propene/butene feedstock by preparing a butene-rich fraction, and treating the butene-rich fraction to provide an n-butene rich fraction.

14. A method as specified in any one of claims 1 to 13, in which the octene fraction is recovered and fractionated prior to oxonation and hydrogenation.

15. The use of an octene obtained in dimerization of butene over a solid phosphoric acid catalyst and having less than 15% triple branching.

16. A nonyl alcohol, obtained by the method as claimed in claim 15.

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17. An ester obtained by the esterification of the nonyl alcohol of claim 16.

18. An ester according to claim 17 in which the alcohol is esterified with phthalic acid or a derivative thereof.

19. A polymeric composition comprising a polymer and the ester of claim 18.

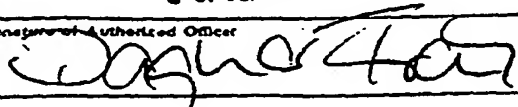
20. A composition as claimed in claim 19, wherein the polymer is a vinyl chloride homo or copolymer.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 92/00245

I. CLASSIFICATION OF SUBJECT MATTER (If several classifications apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ^S : C 07 C 31/125, C 07 C 29/16, C 07 C 69/80, C 08 K 5/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched *		
Classification System (Classification Symbols	
IPC ^S	C 07 C 31/00, C 07 C 29/00, C 07 C 2/00, C 07 C 69/00, C 08 K	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
A	EP, A2, 0 278 407 (MITSUBISHI CHEMICAL) 17 August 1988 (17.08.88), see claim 1; example 1.	1
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A	US, A, 4 229 586 (DENNIS J. WARD) 21 October 1980 (21.10.80), see claims 1,3,5.	1,17, 18
A	US, A, 4 123 471 (NATALE BERTOLINI et al.) 31 October 1978 (31.10.78), see	1
<p>* Special categories of cited documents: **</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
02 April 1992		06.05.92
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		

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Mme Dagmar FRANK

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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A	US, A, 4 291 127 (HIROSHI AKABAYASHI et al.) 22 September 1981 (22.09.81), see column 1, lines 35-42; example 1; claim 1. ---	1,17- 20
A	Patent Abstracts of Japan, unexamined applications, C section, vol. 3, no. 109, September 12, 1979, The Patent Office Japanese Go- vernment, Kokai-no. 54-88 206 (NISSAN KAGAKU KOGYO K.K.), see abstract. ---	1
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Form PCT/ISA 210 (extra sheet) (January 1985)

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/EP 92/00245 SAE 55769

In diesem Anhang sind die Mitglieder
der Patentfamilien der in obenge-
nannten internationalen Recherchenbericht
angeführten Patentedokumente angegeben.
Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
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US A	4123471	31-10-78	keine - none - rien	
GB A	1531660	08-11-78	BR A 7704945 CA A1 1081262 DE A1 2733592 FR A1 2376834 FR B1 2376834 IT A 1074653 JP A2 53087302 MX U 5057	03-04-79 08-07-80 13-07-78 04-08-78 10-10-80 20-04-85 01-08-78 08-03-83
US A	4291127	22-09-81	DE A1 2855421 DE C2 2855421 GB A1 2010857 GB B2 2010857 JP A2 54088236 JP B4 58047410	05-07-79 05-03-87 04-07-79 31-03-82 13-07-79 22-10-83
GB A	477128		keine - none - rien	